Journal of Chromatography, 396 (1987) 43–50
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 19 452

ELECTROMIGRATION OF CARRIER-FREE RADIONUCLIDES

III. OXALATE AND TARTRATE COMPLEXES OF YTTERBIUM(III) IN AQUEOUS SOLUTION

F. RÖSCH*, TRAN KIM HUNG, M. MILANOV, N. A. LEBEDEV and V. A. KHALKIN
Laboratory of Nuclear Problems, Department of Radiochemistry, Joint Institute for Nuclear Research, Dubna, Head Post Office, P.O. Box 79, 10 1000 Moscow (U.S.S.R)

(First received November 4th, 1986; revised manuscript received January 27th, 1987)

SUMMARY

The dependences of the overall ionic mobilities, $\bar{u}$, of Yb(III) on the oxalate ($C_2O_4^{2-}$) and tartrate ($C_4H_4O_6^{2-}$) concentrations in aqueous nitrate electrolytes of overall ionic strength 0.01 and temperature 298.1(1)K were obtained by direct measurements of the electromigration mobilities of carrier-free ^{169}Yb-Yb(III). Mathematical processing of the experimental data allowed the individual concentration constants of Yb(III) to be determined: $[Yb(C_2O_4)]^+$, log K_1 = 5.80(5); $[Yb(C_2O_4)_2]^-$, log K_2 = 4.06(3); $[Yb(C_4H_4O_6)]^+$, log K_1 = 4.61(6). The individual ionic mobilities, u_i^0, of the ions were $u^0_{Yb^{3+}} = +6.01(5) \cdot 10^{-4}$ cm^2 s^{-1} V^{-1}, $u^0_{[Yb(C_2O_4)]^+} = +2.5(2) \cdot 10^{-4}$ cm^2 s^{-1} V^{-1}, $u^0_{[Yb(C_2O_4)_2]^-} = -2.5(1) \cdot 10^{-4}$ cm^2 s^{-1} V^{-1}, $u^0_{[Yb(C_4H_4O_6)]^+} = +2.3(5) \cdot 10^{-4}$ cm^2 s^{-1} V^{-1}. It is shown that Yb(III) is not hydrolysed in neutral (pH $<$ 8) solutions.

INTRODUCTION

The formation of complexes of rare-earth elements with organic ligands in aqueous solutions has often been investigated by electrophoresis. The results and methodical problems have been reviewed[1–3]. In these investigations, electromigration of radionuclides was studied in electrolyte solutions, stabilized by papers, thin layers, gels, finely divided powders, etc., to eliminate convective flows of liquids. Under these conditions there are some drawbacks, *e.g.*, see ref. 2, p. 126, which affect the reproducibility of results. To eliminate them, we have developed an electromigration cell for determination of ion mobilities of carrier-free radionuclides in electrolytes free of supporting materials (Fig. 1). The special features of its design are, first, continuous removal of electrolysis products from the electrode chambers, which ensures a constant electrolyte composition in the electromigration tube, and, secondly, connection of the electromigration tube to the electrode chambers via hydrodynamic resistors, thereby excluding convective flows of liquid. The experimental set-up was described in detail in earlier articles[4–6].

0021-9673/87/$03.50

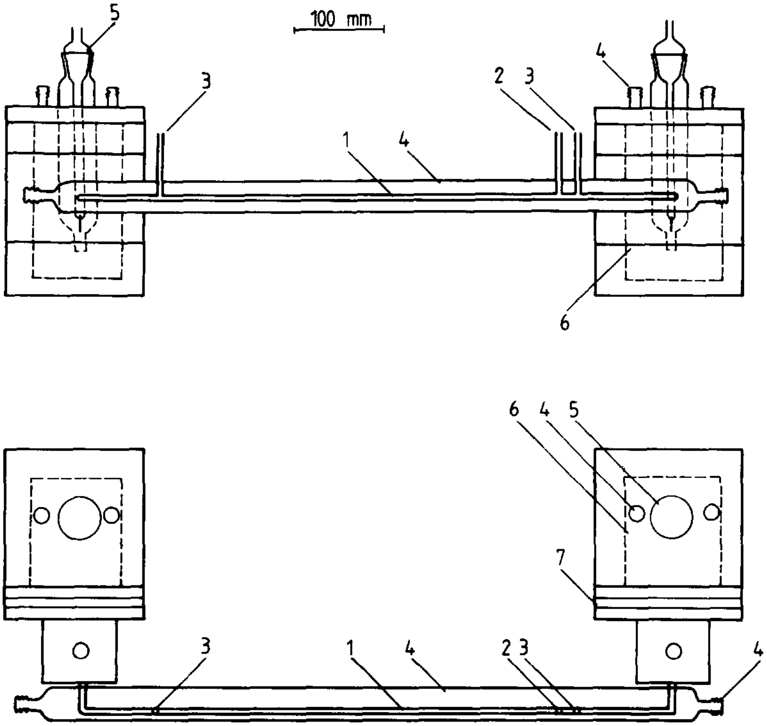

Fig. 1. Schematic view of the electromigration cell: 1 = electromigration tube, 2,3 = inlets of the electromigration tubes for radioactive stock solution of the element under investigation (2) and for the temperature sensor and electrodes for the electric field strength measurement (3); 4 = connection pipes for water to thermostat the electrolytes in the tube and chambers; 5 = platinum electrodes to apply high voltage; 6 = electrode chambers; 7 = flanges to fix hydrodynamic resistors.

The electromigration facility for direct measurement of ion mobilities in electrolyte solutions, equipped with a cell of a new design, was tested by applying it to investigations of bismuth hydrolysis[7]. The good agreement between the results obtained and the available literature data suggested that the technique could be employed in investigations of other processes, including the formation of metal ion complexes with organic ligands. To test this assumption, the radionuclide ^{169}Yb was selected since Yb^{3+} forms stable and well known complexes with oxalate and tartrate anions[8–12]. Data on their stability constants are summarized in Table I.

However, there are no electromigration data on the hydrolysis of Yb^{3+}, which are indispensable when planning complex-formation experiments. Moreover, earlier electrophoresis data[13] on the first hydrolysis constants of Y^{3+}, Ce^{3+} and Nd^{3+} differed by 4–5 orders of magnitude from the results obtained by other authors. We therefore considered it useful to measure the mobilities of Yb^{3+} over a wide range of pH.

TABLE I

STABILITY CONSTANTS OF OXALATE ($C_2O_4^{2-}$) AND TARTRATE ($C_4H_4O_6^{2-}$) COMPLEXES OF Yb(III) IN AQUEOUS SOLUTION

Complex	μ	*T(K)*	*log* K_n^μ	*Ref.*
$[Yb(C_2O_4)]^+$	0	298.1	7.30	8,9
$[Yb(C_2O_4)_2]^-$	0	298.1	4.59	8,9
$[Yb(C_2O_4)_3]^{3-}$	0	298.1	−1.96	8.9
$[Yb(C_4H_4O_6)]^+$	0.2	296.1-298.1	3.48(3)	10
$[Yb(C_4H_4O_6)]^+$	0.05	298.1	4.26(10)	11
$[Yb(C_4H_4O_6)]^+$	0	298.1	5.29	11
$[Yb(C_4H_4O_6)]^+$	0.1	293.1	4.58(49)	12
$[Yb(C_4H_4O_6)_2]^-$	0.1	298.1	3.04	12

EXPERIMENTAL

A radioactive sample of ^{169}Yb ($T_{1/2}$ = 32 d) in $H(K)NO_3$ solution was used. The radionuclide was obtained by exposure of an ytterbium target, enriched with ^{168}Yb (20%), to an intense neutron flux ($2 \cdot 10^{14}$ n cm^{-2} s^{-1}) in the SM-2 reactor, INNAR, Dmitrovgrad, U.S.S.R. The specific activity was of the order of 1 mCi g^{-1}. Ytterbium was separated from contaminations by means of cation-exchange chromatography using solutions of ammonium α-hydroxybutyrate[14]. The latter reagent was removed from the ytterbium solution after purification by evaporation to dryness with nitric acid.

A detailed description of the electromigration procedure is given in refs. 4–7. The electromigration cell (Fig. 1) was filled with electrolyte solution, together with 1–5 μl of the radioactive stock solution of ^{169}Yb-YB(III) final concentration about 10^{-8} *M* in $H(K)NO_3$ whose overall ionic strength, μ, and pH were similar to those of the electrolyte systems. The ionic mobilities of Yb(III) were determined at T = 298.1(1)K and a constant voltage gradient, ΔE = 10.0(1) V cm^{-1} in the following electrolyte systems of constant overall ionic strength $\mu = 0.01$: (i) HNO_3–K_2L, pH 2–3; (ii) $H(K)MO_3$–K_2L, pH ≈ 5.5; (iii) $H(K)NO_3$–K_2L, $2 < pH < 5.5$; (iv) $H(K)NO_3$–KOH, $2 < pH < 12$, where H_2L is oxalic or tartaric acid, respectively. Some determinations in the electrolyte system (iv) were carried out at $\mu = 0.1$ as well as with 10^{-5} *M* Yb(III) as a carrier. The concentrations of oxalate and tartrate were calculated by using concentration dissociation constants of $pK_1 = 1.31$, $pK_2 = 3.81$[15], and $pK_1 = 2.99$, $pK_2 = 4.81$[16], respectively. Twice distilled water and chemically pure reagents were used to prepare electrolyte solutions.

RESULTS

Hydrolysis of Yb(III)

The constant value of the ion mobility, $u_{Yb^{3+}} = +6.03(22) \cdot 10^{-4}\,cm^2\,s^{-1}\,V^{-1}$, measured in electrolyte system (iv) at $2 < pH < 8.5$ (Fig. 2) indicates that Yb^{3+} is not hydrolysed in this range of hydrogen-ion concentration. Consequently, the mole

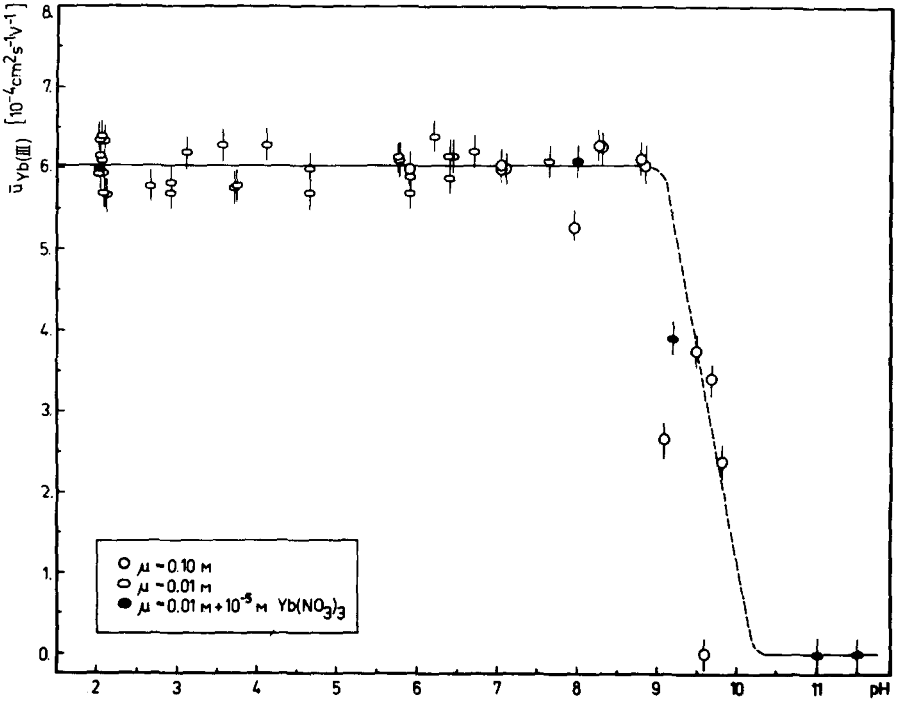

Fig. 2. Plot of ytterbium(III) overall ionic mobility against the pH of aqueous nitrate solutions of electrolyte system (iv); $T = 298.1(1)$ K.

fraction of Yb^{3+} in respect of the hydrolysis of Yb(III) is $\alpha_{Yb^{3+}} = 1$. In weak alkaline solutions with pH 9–10 the element is adsorbed to the glass surface of the electromigration tube. This effect leads to disturbance of the hydrolysis equilibrium and, consequently, to irreproducible results. However, an analysis of the experimental electromigration data, shown in Fig. 2, indicates that $pK_1 \approx 9$ for the first hydrolysis constant of Yb(III). This value is of the same order of magnitude as the constants of Yb(III) and other trivalent lanthanides determined by methods other than electrophoresis[13].

Oxalate complexes of Yb(III)

The overall ion mobility, $\bar{u}$, of ytterbium(III) changes with the concentration of oxalate ion (Fig. 3) in similar manner whether in acid (pH 2–3) and neutral solutions (pH $\approx$ 5.5). This can be regarded, first, as confirmation of the conclusion that Yb(III) is not hydrolysed in neutral solutions (Fig. 2), and, secondly, as an indication of the formation of relatively weak complexes of ytterbium(III) with $HC_2O_4^-$. With $[C_2O_4^{2-}]$ 10^{-4} M, the overall ionic mobility of Yb(III) is negative. This indicates the formation of complex anions $[Yb(C_2O_4)_n]^{3-2n}$ with $n > 1$.

When interpreting the experimental electromigration data, the formation of oxalate complexes through reaction 1 is assumed

$$Yb^{3+} + nC_2O_4^{2-} \overset{\beta_n}{\rightleftharpoons} [Yb(C_2O_4)_n]^{3-2n} \qquad (1)$$

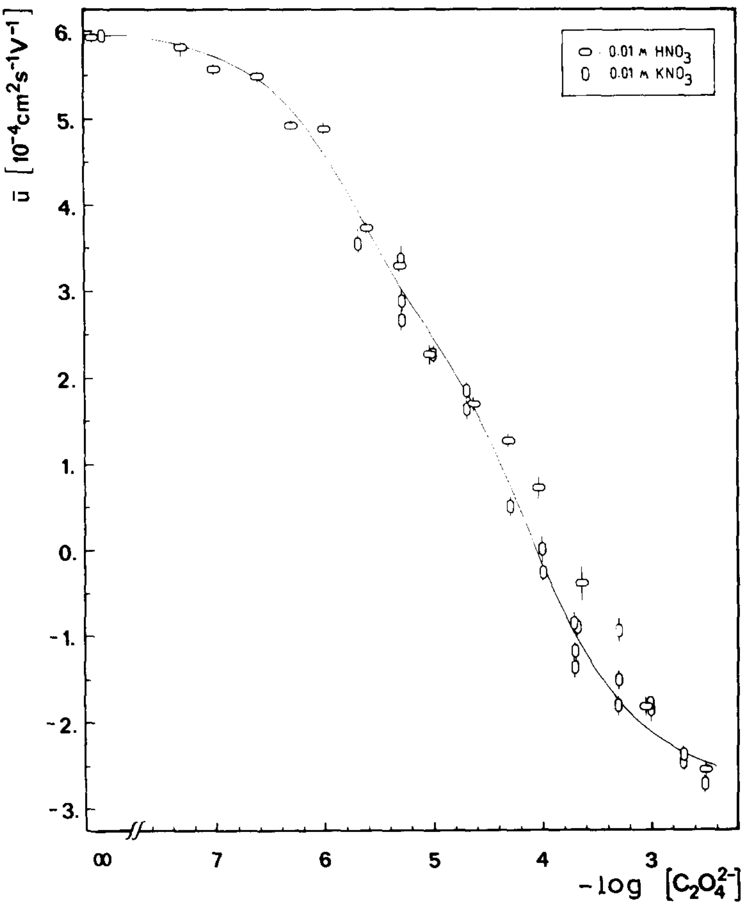

Fig. 3. Plot ytterbium(III) overall ionic mobility against the oxalate-ion concentration in aqueous nitrate solutions of electrolyte systems (i), (ii); $T = 298.1(1)$ K.

where $n = 1.2$. According to reaction 1, the overall ionic mobility of ytterbium(III) in oxalate solutions will be described by

$$\bar{u}_{\mathrm{Yb(III)}} = \frac{u^0_{\mathrm{Yb}^{3+}} + u^0_{\mathrm{YbL}^+}K_1[\mathrm{L}^{2-}] + u^0_{\mathrm{YbL}_2^-}K_1K_2[\mathrm{L}^{2-}]^2}{1 + K_1[\mathrm{L}^{2-}] + K_1K_2[\mathrm{L}^{2-}]^2} \tag{2}$$

where u_i^0 are the individual ionic mobilities of species $[\mathrm{YbL}_n]^{3-2n}$, $n = 0,1,2$, K_1 and K_2 are the individual concentration constants of the complex formation and $[\mathrm{L}^{2-}]$ is the concentration of the ligand, *i.e.*, in this case oxalate.

The dependences $\bar{u}_{\mathrm{Yb(III)}} = \mathrm{f}([\mathrm{L}^{2-}])$, obtained experimentally, were processed mathematically according to eqn. 2 by a least squares method using the computer program MINUIT[17]. The results of the measurements, performed in electrolyte systems (i) and (ii), were pooled. The calculation results are listed in Table II. The line

TABLE II

INDIVIDUAL CONCENTRATION CONSTANTS AND IONIC MOBILITIES OF $[YbL_n]^{3-2n}$ (L = OXALATE OR TARTRATE), CALCULATED ON THE BASIS OF EXPERIMENTAL DEPENDENCES $\bar{u}_{Yb(III)}$ = f([L^{2-}]), μ = 0.01; T = 298.1(1) K

Ion	*log K_n (K_n in l mol^{-1})*	*u_i^0 (10^{-4} cm^2 s^{-1} V^{-1})*
Yb^{3+}	–	+5.92(8)
$[Yb(C_2O_4)]^+$	5.80(5)	+2.49(24)
$[Yb(C_2O_4)_2]^-$	4.06(3)	−2.53(10)
Yb^{3+}	–	+5.98(8)
$[Yb(C_4H_4C_6)]^+$	4.61(6)	+2.25(53)

drawn in Fig. 3 shows the function $\bar{u}_{Yb(III)}$ = f([$C_2O_4^{2-}$], u_i^0, K_n), calculated by eqn. 2 using u_i^0 and K_n data from Table II.

Tartrate complexes of Yb(III)

The dependences of the overall ionic mobility of Yb(III) on the tartrate concentration in electrolytes (i)–(iii) are shown in Fig. 4. As in oxalate solutions, the concentration of hydrogen ions does not affect the overall ytterbium mobility, indicating the absence of formation of hydrogentartrate complexes.

In the tartrate concentration interval investigated the measured overall ionic mobilities were positive. This can be interpreted as negligible formation of the anionic complex $[Yb(C_4H_4O_6)_2]^-$. However, in order to haver an opportunity of mathematically processing the experimental data of Fig. 4 according to eqn. 2, we had to

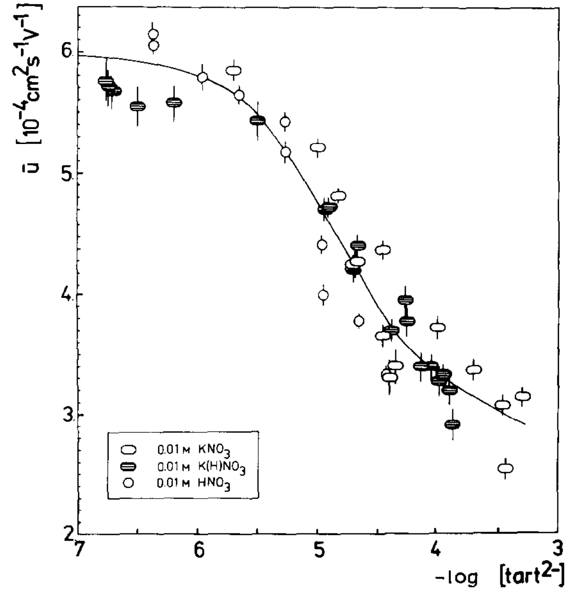

Fig. 4. Plot of ytterbium(III) overall ionic mobility against the tartrate-ion concentration in aqueous nitrate solutions of electrolyte systems (i)–(iii); T = 298.1(1) K.

take the individual ionic mobility of $[Yb(C_4H_4O_6)_2]^-$ as equal to that of the similar oxalate complex: $u^0_{YbL_2^-} = -2.5(5) \cdot 10^{-4}\ cm^2\ s^{-1}\ V^{4-1}$. The calculation results are given in Table II. The curve shown in Fig. 4 is the dependence $\bar{u}_{Yb(III)} = f([C_4H_4O_6^{2-}], u_i^0, K_n)$ calculated using the values of u_i^0 and K_n obtained.

DISCUSSION

Table I lists the individual thermodynamic stability constants of oxalato complexes of Yb(III), based on solubility experiments[8,9]. For comparison, our concentration constants were extrapolated to a value of $\mu = 0$ using Davies' empirical formula[18,19]:

$$\log K_n^0 = \log K_n^\mu - \Delta Z^2 \cdot A\left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2\mu\right) \tag{3}$$

In our case $\Delta Z^2 = -12$ and -4 for calculation of $\log K_1^0$ and $\log K_2^0$ respectively; A is the Debye-Hückel coefficient, 0.511 for aqueous solutions at 298.1K.

The extrapolated values of $\log K_1^0 = 6.34(5)$ and $\log K_2^0 = 4.24(5)$ are in satisfactory agreement with the results in refs. 8 and 9, taking into account the principal differences in the analytical technique and related assumptions.

The $\log K_1 = 5.15(6)$ value for the tartrato complex of Yb(III), obtained in the present work is in better agreement with literature data. Values of Table I extrapolated to $\log K_1^0$ are 5.12(3)[10,11], 5.29[11], 5.29(49)[12].

These results demonstrate that the special electromigration technique involving direct measurement of ionic mobilities of radionuclides in homogeneous aqueous electrolytes readily yields well reproducible experimental data on the complex formation of metal ions, necessary for calculation of reliable values of equilibrium constants.

Additionally, new and interesting data on the individual ionic mobilities of $[YbL_n]^{3-2n}$, $n = 0,1,2$ are provided. First of all, the constant ionic mobility of Yb(III) showed that Yb(III) is not hydrolysed in aqueous solutions with pH < 8, $\mu = 0.01$–0.1, $T = 298.1$ K. A mean individual ionic mobility of $u^0_{Yb^{3+}} = +6.03(22) \cdot 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$ has been determined in electrolyte (iv). Similar values for $u^0_{Yb^{3+}}$ were obtained by mathematical processing of the dependences of the overall mobility of Yb(III) in oxalate and tartrate solutions, giving a final value of $u^0_{Yb^{3+}} = +6.01(5) \cdot 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$ in $\mu = 0.01$ nitrate solutions. The calculated individual ion mobilities $u^0_{YbL^+}$ and $u^0_{YbL_2^-}$ are practically the same. The ratios of $u^0_{Yb^{3+}}$ to $u^0_{YbL^+}$ and $u^0_{YbL_2^-}$, respectively, are almost 3:1 (actually 2.34 for oxalate and 2.66 for tartrate). This allows a tentative conclusion that the main factor affecting the migration mobilities of complex ions of a metal cation with organic ligands like oxalate and tartrate is its charge.

REFERENCES

1 V. P. Shvedov (Editor), *Electromigration Method in Physicochemical and Radiochemical Investigations* (in Russian), Atomizdat, Moscow, 1971.
2 T. P. Makarova and A. V. Stepanov, *Radiokhimiya*, 19 (1977) 125.
3 A. V. Stepanov and E. K. Kortshemnaja, *Electromigration Method in Inorganic Analysis* (in Russian), Khimiya, Moscow, 1979.
4 M. Milanov, W. Doberenz, A. Marinov and V. A. Khalkin, *J. Radioanal. Nucl. Chem.*, 82 (1981) 101.
5 M. Milanov, W. Doberenz, R. Dreyer, M. Noak and V. A. Khalkin, *Radiokhimiya*, 24 (1982) 520.
6 M. Milanov, A. Marinov, Tran Kim Hung, W. Doberenz, N. I. Zhuravlev, A. V. Salamatin, D. Vassilev and V. A. Khalkin, *JINR 6-83-209*, Joint Institute of Nuclear Research, Dubna, 1983.
7 M. Milanov, F. Rösch, J. Henniger, V. A. Khalkin and Tran Kim Hung, *JINR E12-86-144*, Joint Institute of Nuclear Research, Dubna, 1986.
8 C. E. Crouthamel and D. S. Martin, *J. Am. Chem. Soc.*, 72 (1950) 1382.
9 C. E. Crouthamel and D. S. Martin, *J. Am. Chem. Soc.*, 73 (1951) 569.
10 N. K. Davidenko and V. F. Deribon, *Zh. Neorg. Khim.*, 11 (1966) 99.
11 G. N. Shabanova and N. A. Skorik, *Zh. Obshch. Khim.*, 42 (1972) 204.
12 N. K. Dobrynina, L. N. Martynenko and V. I. Spizin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 10 (1968) 2203.
13 V. A. Nazarenko, V. P. Antonovich and E. M. Nevskaja, *Metal Ions Hydrolysis in Dilute Solutions* (in Russian), Atomizdat, Moscow, 1979, p. 62.
14 V. A. Khalkin and N. A. Lebedev, *J. Radioanal. Nucl. Chem.*, 88 (1985) 155.
15 G. M. Armitage and H. S. Dunsmore, *J. Inorg. Nucl. Chem.*, 35 (1973) 817.
16 T. B. Komunova and L. S. Kachkov, *Z. Neorg. Khim.*, 18 (1973) 1527.
17 F. James and M. Roos, *CERN Computer 6000 Series Program Library*, Long-Write-Up D 506, D 516 (1971).
18 C. W. Davies, *Ion Association*, Butterworth, London, 1962, p. 39.
19 V. P. Vasiliev, *Thermodynamic Properties of Electrolyte Solutions* (in Russian), Vysch. Shkola, Moscow, 1982, p. 261.